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KINETIC INVESTIGATION OF THE ATOM TRANSFER RADICAL  
POLYMERIZATION OF STYRENE IN HOMOGENEOUS SYSTEMS

by

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# Kinetic Investigation of the Atom Transfer Radical Polymerization of Styrene in Homogeneous Systems

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## INTRODUCTION

Living polymerization is a chain polymerization process in which there is neither chain transfer nor termination.<sup>1</sup> Polymers with low polydispersities and complex architectures can be prepared by a living polymerization process. Until recently, most of the living polymerization systems were reported for anionic,<sup>2,3</sup> cationic<sup>4</sup> and group transfer polymerizations.<sup>5</sup> However, the industrial application of these techniques have been limited by the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions. In contrast, free radical polymerization process is easy to operate and can be readily performed in bulk or solution. Recently, we reported the transition metal catalyzed atom transfer radical polymerization (ATRP),<sup>6</sup> a novel controlled/"living" radical process in which polymers with predetermined molecular weight up to  $M_n \approx 10^5$  and polydispersity as narrow as 1.05 have been obtained.<sup>7</sup> Kinetic studies with styrene using 2,2'-dipyridyl as the ligand indicated that the polymerization proceeded first order with respect to the concentration of initiator, and was 0.4 and 0.6 orders with respect to the concentration of Cu(I) halide and ligand.<sup>8</sup> However the heterogeneity of the system made it difficult to explain the precise physical meanings for the fractional orders observed. By using alkyl substituted bipy ligands, such as 4,4'-di-(5-nonyl)-2,2'-dipyridyl (NBPY) and 4,4'-di-n-heptyl-2,2'-dipyridyl (HBPY), homogeneous ATRP can be achieved. In this paper, we report a kinetic investigation of the ATRP of styrene under such homogeneous conditions.

## EXPERIMENTAL

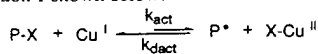
**Materials:** Styrene was vacuum distilled from CaH<sub>2</sub> before polymerization. CuBr (98%, Aldrich), CuCl (98%, Aldrich) were purified according to the published procedure.<sup>9</sup> Phenyl ether (ACROS), used as the solvent, was purged with argon for 15 min before polymerization. Ligands 4,4'-di-(5-nonyl)-2,2'-dipyridyl (NBPY) was obtained from Reilly Industries, and 4,4'-di-n-heptyl-2,2'-dipyridyl (HBPY) was synthesized according to the procedure of Kramer, *et al.*<sup>10</sup> Initiators 1-phenylethyl bromide (1-PEBr) and 1-phenylethyl chloride (1-PECl) were obtained from Aldrich and used as received.

**Polymerization:** The general procedure for the polymerization was as follows. To a degassed dry Schlenk flask with copper halide and ligand were added the degassed solvent and monomer, followed by the addition of the initiator. The reaction mixture was immersed in a thermostated oil bath and allowed to stir till it was homogeneous, then a 0.5 ml sample of the solution was withdrawn using a degassed syringe and added to 2.5 ml THF as the time = 0 data point. At the timed interval, a 0.5 ml solution sample was taken from the reaction mixture as described above.

**Characterization:** Monomer conversion was determined by GC using THF as an internal standard. Molecular weight and molecular weight distribution were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å and 100 Å. Polystyrene standards were used to calibrate the columns.

## RESULTS AND DISCUSSION

The kinetic analyses are based upon the rate law for ATRP as given by Equation 1 shown below:



$$K_0 = \frac{k_{act}}{k_{dact}} = \frac{[P^\bullet][X-Cu^{II}]}{[Cu^I][P-X]}$$

$$R_p = k_p [M][P^\bullet] = k_p K_0 [M][I] \frac{[Cu^I]}{[X-Cu^{II}]} = k_p^{app} [M] \quad (1)$$

### (1). Reaction order with respect to initiators: 1-PEBr & 1-PECl

Figures 1 and 2 illustrate the kinetic data obtained for a series of polymerizations using as initiators 1-PEBr at 110 °C and 1-PECl at 130 °C respectively. The concentration of monomer, copper halide and bipy ligand were held constant at 4.34 M,  $4.5 \times 10^{-2}$  M and  $9.0 \times 10^{-2}$  M, respectively.

Each line represents a different  $[monomer]_0$  to  $[initiator]_0$  ratio, i.e., a different target molecular weight, and the slope is equal to  $k_p^{app}$ , the apparent propagation rate constant ( $k_p^{app} = d \ln[M]/dt$ ). The linearity of the plots shows the polymerization followed first order kinetics with respect to the monomer and that the concentration of growing radicals remained constant for both initiators. By plotting  $\ln(k_p^{app})$  vs.  $\ln[initiator]_0$  as shown in Figure 3, it was determined that the rate of polymerization is first order with respect to the concentration of both initiators. It seems that the overall rates in RCl/CuCl system are slower and at 130 °C are similar to those in RBr/CuBr system at 110 °C.

### (2). Reaction order with respect to Cu(I) halide: CuBr & CuCl

Figure 4 depicts the effect on the polymerization rate of Cu(I) halide concentration with all other components held constant. A plot of  $\ln(k_p^{app})$  vs.  $\ln[CuX]_0$  reveals that the rate of polymerization varies with the concentration of both Cu(I) halides approximately to the first power. Slightly lower order for CuCl may be due to either its low solubility or higher tendency to form dimers.

### (3). Effect of Cu(II) halide:

A series of polymerizations was performed by adding a predetermined amount of CuBr<sub>2</sub> into the polymerization mixture to investigate the effect of Cu(II) halide. By plotting  $\ln(k_p^{app})$  vs.  $\ln[CuBr_2]_0$  as shown in Figure 5, it was determined that the rate of polymerization is proportional to the 0.25 power of the reciprocal of the CuBr<sub>2</sub> concentration. The amount of CuBr<sub>2</sub> added was calculated from the volume of a CuBr<sub>2</sub> solution taken from a CuBr<sub>2</sub> stock solution in styrene. It was noticed however that the stock solution was not completely homogeneous and thus would presumably induce some deviation of the reaction order with respect to Cu(II) halide, as indicated by the poor correlation coefficient. The other possibility, currently being studied, is that CuBr<sub>2</sub> can react with styrene to form 1,2-dibromo adduct and CuBr which acts as an activator. Additionally, externally added CuBr<sub>2</sub> reacts only with free radicals and may not affect reactions occurring in the "cage".

### (4). Effect of the $[ligand]_0/[CuX]_0$ ratio

To gain better insight into the possible active Cu(I) species in ATRP, a series of polymerizations was performed by varying the concentration of the bipy ligand while keeping the concentration of monomer, initiator and Cu(I) halide constant. A plot of  $\ln(k_p^{app})$  vs.  $\ln([ligand]_0/[CuX]_0)$  as shown in Figure 6 reveals that the kinetic order with respect to the bipy ligand is 1.1. Of the three possible Cu(I) complexes shown in Scheme 1, data from Figure 6 show that Cu(I)L<sub>2</sub> is the most active species and there is a small amount of **B** at  $[ligand]_0 > 2[CuX]_0$ .

### (5). Temperature effect

Figure 7 shows the effect of temperature on the rate of polymerization. From the slope it was estimated that the enthalpy changes between the dormant and active species are  $\approx 0$  kJ/mol and  $\approx 25$  kJ/mol for bromide and chloride based systems respectively.

## CONCLUSIONS

In summary, it was determined from this investigation that the ATRP of styrene under homogeneous conditions is first order with respect to the concentration of monomer, initiator and Cu(I) halide. When the reaction order was determined with respect to the reciprocal of Cu(II) halide concentration, a value of 0.24 was calculated. The low solubility of Cu(II) halide could partially be responsible for the deviation from the first order. The results also showed that Cu(I)L<sub>2</sub> is the most active copper complex in ATRP.

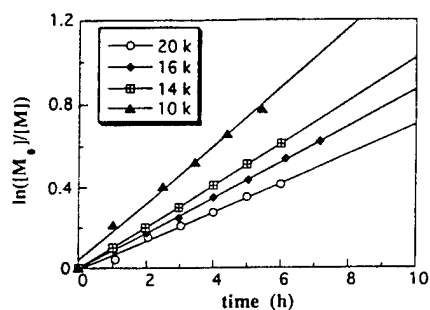
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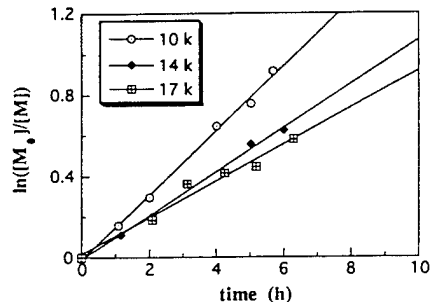
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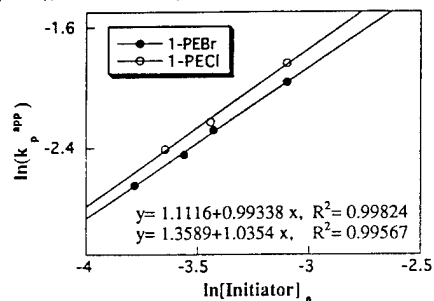
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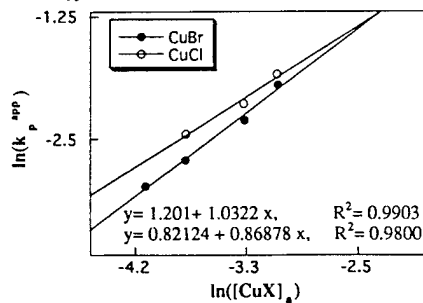
**Figure 1:** Effect of  $[1\text{-PEBr}]_0$  on the ATRP of styrene at 110 °C in  $\text{Ph}_2\text{O}$ .  $[\text{styrene}]_0 = 4.34 \text{ M}$ ;  $[\text{CuBr}]_0 = [\text{NBPy}]_0/2 = 4.5 \times 10^{-2} \text{ M}$ ;  $[1\text{-PEBr}]_0 = 4.5 \times 10^{-2} \text{ M}$  (10 K),  $3.2 \times 10^{-2} \text{ M}$  (14 K),  $2.8 \times 10^{-2} \text{ M}$  (16 K),  $2.26 \times 10^{-2} \text{ M}$  (20 K).



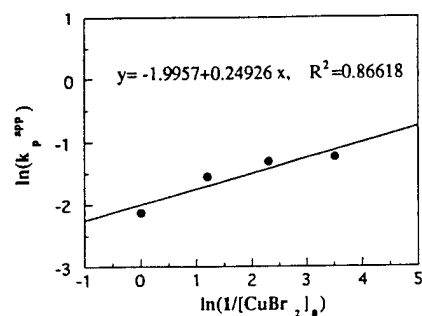
**Figure 2:** Effect of  $[1\text{-PECl}]_0$  on the ATRP of styrene at 130 °C in  $\text{Ph}_2\text{O}$ .  $[\text{styrene}]_0 = 4.34 \text{ M}$ ;  $[\text{CuCl}]_0 = [\text{NBPy}]_0/2 = 4.5 \times 10^{-2} \text{ M}$ ;  $[1\text{-PECl}]_0 = 4.5 \times 10^{-2} \text{ M}$  (10 K),  $3.2 \times 10^{-2} \text{ M}$  (14 K),  $2.6 \times 10^{-2} \text{ M}$  (17 K).



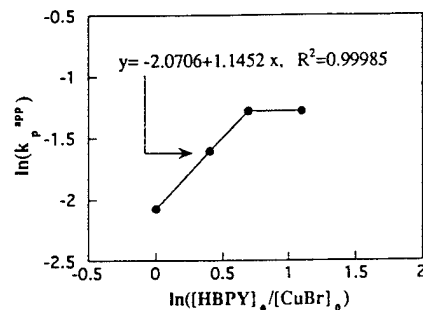
**Figure 3:** Reaction orders for initiators 1-PEBr (110 °C) and 1-PECl (130 °C) in the ATRP of styrene in  $\text{Ph}_2\text{O}$ .  $[\text{styrene}]_0 = 4.34 \text{ M}$ ;  $[\text{CuX}]_0 = [\text{NBPy}]_0/2 = 4.5 \times 10^{-2} \text{ M}$ .



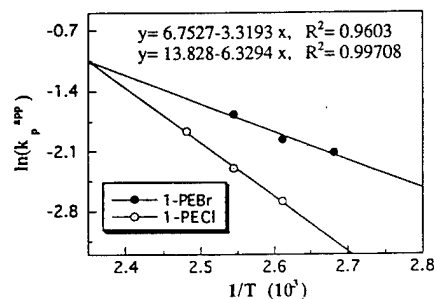
**Figure 4:** Reaction orders for CuBr (110 °C) and CuCl (130 °C) in the ATRP of styrene in  $\text{Ph}_2\text{O}$ .  $[\text{styrene}]_0 = 4.34 \text{ M}$ ;  $[1\text{-PEX}]_0 = [\text{NBPy}]_0/2 = 4.5 \times 10^{-2} \text{ M}$ .



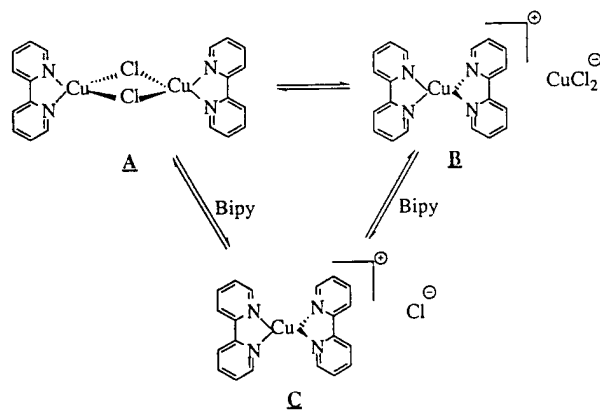
**Figure 5:** Reaction orders for  $\text{CuBr}_2$  (110 °C) in the ATRP of styrene in bulk.  $[1\text{-PEBr}]_0 = [\text{CuBr}]_0 = [\text{HBPy}]_0/2 = 0.1 \text{ M}$ .



**Figure 6:** Reaction orders for ligand in the ATRP of styrene in bulk at 110 °C.  $[1\text{-PEBr}]_0 = [\text{CuBr}]_0 = 0.1 \text{ M}$ .



**Figure 7:** Temperature dependence in the ATRP of styrene in  $\text{Ph}_2\text{O}$ .  $[1\text{-PEX}]_0 = [\text{CuX}]_0 = [\text{NBPy}]_0/2 = 4.5 \times 10^{-2} \text{ M}$ .



**Scheme 1:** Possible Cu(I) species in the ATRP solution.